



TITLE:

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CITATION:

Nakano, Takato. Mechanism of microfibril contraction and anisotropic dimensional changes for cells in wood treated with aqueous NaOH solution. Cellulose 2010, 17(4): 711-719

ISSUE DATE:

2010-08

URL:

<http://hdl.handle.net/2433/126692>

RIGHT:

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**Mechanism of microfibril contraction and anisotropic dimensional changes
for cells in wood treated with aqueous NaOH solution**

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Key words: anisotropic dimensional change, microfibril, sodium hydroxide solution, swelling,
shrinking, cell wall

Received **, ****; accepted **, ****

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Abstract

Anisotropic swelling of wood samples was observed upon treatment with an aqueous NaOH solution with 0 to 0.20 fraction concentrations. At NaOH concentrations less than 0.10, the swelling occurred only along the tangential axis (T) and not along the radial (R) or longitudinal (L) axes. At greater NaOH levels, the swelling was even more pronounced along T with shrinkage along the other axes. These anisotropic changes along R and L were closely related to the crystallinity of microfibrils in the wood cell wall and simulated with a cell structure model. This exercise revealed microfibril contraction and matrix swelling in the wood cell wall upon NaOH treatment. The observed anisotropy in cross section was caused by differences in the microfibril angles (LR and LT) with the cell wall.

Introduction

Wood samples treated with aqueous NaOH show characteristic dimensional change, especially interesting along the longitudinal axis. Stöckmann (1971a, 1971b) discussed this phenomenon in detail and thermodynamically characterized the contraction of microfibrils in the wood cell wall, though the contraction mechanism of microfibrils themselves was not clarified. This contraction along the longitudinal axis is also induced by other alkaline solutions, the degree of which increases as $\text{NaOH} < \text{KOH} < \text{LiOH}$ at the same concentration (Nakano, 1988a, 1988b, 1989). Nakano *et al.* (2000) found from relaxation behavior and temperature dependence studies that this contraction was due to the entropy elastic force of cell wall microfibrils, and formulated a relationship between the sample length, the microfibril dimensions, and microfibril angle.

Treatment with aqueous alkaline solutions also yields changes along the radial and tangential axes, which are negative and positive, respectively (Stöckmann, 1971a, 1971b), while the sum of their changes remains nearly constant (Ishikura and Nakano, 2007). The mechanism and a quantitative relationship between these anisotropic changes have not yet been elucidated. In the present work, the relationship between changes along all three axes upon exposure of wood samples to aqueous NaOH was established from simulations of a cell wall model. The results reported herein provide information about not only the anisotropic swelling of wood but also about the structure of the wood cell wall.

Material and Methods

The validity of the cell wall model employed herein was examined by comparing experimental data reported by Ishikura and Nakano (2007) with data calculated in the present work. Preparation condition in their report is followed. Yezo spruce, Saghalin fir, and Japanese larch, all soft woods that exhibit small microfibril angles, were prepared. Samples with dimensions of $20(\text{R}) \times 20(\text{T}) \times 0.5(\text{L})$ mm, where R, T, and L correspond to the radial, tangential, and longitudinal axes, were soaked in aqueous NaOH solution with 0 to 0.20 fraction concentrations after drying under vacuum at room temperature over P_2O_5 for four days. The

samples were stored at room temperature for two days and then washed in distilled water for one week. Changes along each axis were calculated from the observed differences between wet dimensions after NaOH treatment and the same measurements after soaking in distilled water without NaOH treatment. Their dimensions were measured by a slide calipers for R and T and a micrometer for L.

The crystallinity of the wood samples were determined from X-ray diffraction data obtained on the LR-plane at 30 kV, 100 mA, and 2 °/min. The degree of crystallinity was calculated from an the diffraction profile in the scanning range 10 – 32°. The profile was isolated to two parts of a non-crystalline and a crystalline, after subtracting air-scattering. The degree of crystallinity was defined as fraction of the crystalline reflection area to the gross area. As for the same samples, microfibril angles were freshly in this work measured by X-ray irradiation to know the effect of NaOH treatment on microfibril angles. In order to have higher precision LR-plane of a sample was measured at 40kV and 30 mA, and then were calculated according to Cave's method.

Results and discussion

Characterization of the dimensional change

Figure 1 represents experimental results, in which NaOH treatment induces dimensional changes not only along the longitudinal axis but also along the radial and tangential axes with $\Delta R/R < \Delta T/T$ in the cross section. At NaOH concentrations, [NaOH], greater than 0.10 fraction concentration, $\Delta R/R$ and $\Delta T/T$ values were less than and greater than zero, respectively. It is clearly found that this anisotropically dimensional change differs from that induced under water adsorption.

A suitable cell model is necessary to discuss the characteristic dimensional changes shown in Fig. 1. Various cell models have been proposed to study features such as the anisotropic swelling and shrinkage of wood and wood cells, including models proposed by Barber and Meylan (1967), Yamamoto (1999), and Neagu and Gamstedt (2007), and the simplified model by Fratzl (2008). Salmèn and Burgert (2009) reviewed recent reports describing cell -wall models. The

modern cell model considers anisotropic microfibrils embedded in an elastic isotropic matrix; the constitutive equation is derived under the equilibrium condition with adsorbed water in which the matrix is isotropically swelling and microfibrils restrict this swelling. The microfiber angle is an important factor for anisotropic dimensional change in the longitudinal direction and perpendicular to the longitudinal direction. That is, the model is cylindrical. On the other hand, Preston (1942) and Sadoh and Kingston (1967) examined anisotropic swelling considering the geometrical deformation due to a swelling factor and some restraint.

Analysis of dimensional change should consider the interaction between microfibrils and the matrix for the anisotropy of a cross-section. A model of equilibrium between the matrix and microfibril restriction appears not to be suitable for simulation of anisotropic dimensional change because there is insufficient information on microfibril movement.

We follow the approach of Sadoh and Kingston (1967) in the discussion below. Dimensional change of the matrix and the microfibrils resulting from both the swelling and restraint induced by NaOH treatment is examined to analyze anisotropic dimensional change. Dimensional change in each direction is merely the sum of both contributions, assuming that the matrix swelling is restricted by an unknown factor which is evaluated by swelling weight, that each dimensional change is independent, and that change in the cell wall thickness is negligible. The above assumptions imply that each dimensional change is described by the geometrical sum of the dimensional change of the microfibrils and that of the matrix with swelling weight.

Our model of anisotropic dimensional change also considers anisotropic microfibrils embedded in an elastic isotropic matrix. Note that microfibrils are contractible and that the microfibril angle is constant with NaOH treatment, as discussed below.

Nakano *et al.* (2000) derived the following equation for the longitudinal contraction of wood treated with aqueous NaOH solution, assuming that distortion of the sample along the longitudinal axis depended on both microfibril contraction and a change in the microfibril angle.

$$\frac{\Delta L}{L} = \frac{\Delta l}{l} + \frac{\Delta \cos \theta}{\cos \theta},$$

where L and l are the sample length along the longitudinal axis and the microfibril length, respectively, $\cos \theta$ is the cosine of the microfibril angle θ , and $\Delta L/L$, $\Delta l/l$ and $\Delta \cos \theta / \cos \theta$ represent the relative change in each of these variables. This equation is essentially the same as

that of microfibrils derived by Sadoh and Kingston (1967) to discuss longitudinal shrinkage of wood. It should be noted that the longitudinal axis of microfibril differs from that of the sample.

Lindström *et al.* (1988) examined the dependence of swelling behavior on [NaOH] for milled wood lignin (MWL), which is the main matrix of wood gelled by epichlorohydrin. They evaluated the swelling of MWL not by dimensional changes but by weight gain. In their report, the water gain (w/w) was maximal at $0.8 < [\text{NaOH}] < 1.6$ meq/g. The amount of weight gain increased gradually with increasing [NaOH] and increased rapidly at $[\text{NaOH}] > 20$ meq/g. This demonstrated that at high NaOH levels, lignin swelling was dependant on NaOH concentration.

Considering dimensional change of the wood matrix with lignin, the above equation is reduced to

$$\frac{\Delta L}{L} = \frac{\Delta l}{l} + \frac{\Delta \cos \theta}{\cos \theta} + K_1 \frac{\Delta m}{m},$$

where $\Delta m / m$ is the swelling ratio of the matrix and K_1 is the swelling weight of matrix along the longitudinal axis of the sample. Restraint of matrix swelling is evaluated by the parameter K_1 , which is probably caused by microfibrils. Figure 2 shows that the microfibril angle for Yezo spruce was on average 8.7° and exhibited no dependence on [NaOH]. The result shown in Figure 2 is different from the result by Fujimoto and Nakano (2000) that the fibril angle depended on [NaOH] using the iodine method. However, the results measured by X-ray irradiation was adopted in this work. This is because the X-ray diffraction method gives the average value of the fibril angles, though the iodine method does the local information for some cell walls. For wood species with very small microfibril angles, such as those used in the current study, where $\Delta \cos \theta = \Delta \theta \cdot \sin \theta \approx 0$, no dependence on [NaOH] was observed. The above equation then reduces to

$$\frac{\Delta L}{L} = \frac{\Delta l}{l} + K_1 \frac{\Delta m}{m}. \quad (1)$$

According to Equation (1), $K_1 \Delta m / m \approx 0$ was expected since the contribution of the wood matrix to the change along the longitudinal direction was much smaller than that of microfibrils because of the high elastic modulus of the microfibrils. However, dimensional changes in wood samples occur not only along the longitudinal axis but also along the radial and tangential axes (Stöckmann, 1971a, 1971b; Ishikura and Nakano, 2007). Due to the small microfibril angle,

changes along the latter axes need to be considered in terms of matrix contributions. That is strikingly different from the dimensional change along the longitudinal axis. We will deal with not the mechanical equilibrium between wood components but the dimensional change resulted from both the swelling and restraint induced with NaOH treatment, as discussed below.

Expressions to describe the changes along the radial and tangential axes were initially derived assuming that the wood cell wall consists of two phases: the cellulose microfibril and an isotropic matrix, with a volume fraction microfibril / matrix = $\phi / (1 - \phi)$, and microfibril angles of the LT- and LR-planes in wood cell wall designated as θ_{LT} and θ_{LR} , respectively. Given this model structure, shown schematically in Figure 3, with a small microfibril angle, the changes along the radial and tangential axes of the sample are represented by

$$\frac{\Delta R}{R} = \phi \frac{\Delta l}{l} \sin \theta_{LR} + K_2 (1 - \phi) \frac{\Delta m}{m}, \quad (2)$$

$$\frac{\Delta T}{T} = \phi \frac{\Delta l}{l} \sin \theta_{LT} + K_3 (1 - \phi) \frac{\Delta m}{m}, \quad (3)$$

where the microfibril change along the longitudinal axis of itself is given by $\Delta l / l$, and dimensional changes along the radial and tangential axes of the sample are given by $\Delta R / R$ and $\Delta T / T$, respectively. Matrix contributions are represented by $\Delta m / m$. K_2 and K_3 are the swelling weight and are related to the anisotropy restraint of the radial and tangential orientations, respectively. or the Poisson ratio effect. If the Poisson ratio effect is different between LT-plane and LR-plane of wood cell due to the longitudinal shrinking as well as that for water sorption (Skaar, 1988), $\Delta T / T$ may be different from $\Delta R / R$. Considering that the microfibril angle is sufficiently small and that $\Delta R / R < \Delta T / T$ over [NaOH] as shown in Fig.1, $0 < K_2 < K_3 < 1$. Dimensional change perpendicular to the longitudinal axis of the microfibrils is neglected in equations (2) and (3) because the contribution of $\Delta l / l$ is greater than that of the change perpendicular to the longitudinal axis of microfibrils. The reason is that the Poisson's ratio is generally 0.3 or less for solid materials.

Changes in sample cross section and microfibril contraction

The following discussion will focus on the implications of these dimensional changes as shown in Figure 1. At $[\text{NaOH}] > 0.10$, the signs in Equations (2) and (3) follow from Figure 1:

$$\frac{\Delta R}{R} = \phi \frac{\Delta l}{l} \sin \theta_{LR} + K_2 (1 - \phi) \frac{\Delta m}{m} < 0, \quad (4)$$

$$\frac{\Delta T}{T} = \phi \frac{\Delta l}{l} \sin \theta_{LT} + K_3 (1 - \phi) \frac{\Delta m}{m} > 0. \quad (5)$$

The sum of multiplying Equation (4) by K_3 and multiplying Equation (5) by $-K_2$ yields

$$\phi \frac{\Delta l}{l} (K_3 \sin \theta_{LR} - K_2 \sin \theta_{LT}) < 0, \quad (6)$$

Considering that $0 < \phi < 1$, $0 < K_2 < K_3 < 1$ and $0 < \theta_{LT} < \theta_{LR} \ll 90^\circ$ so that $(K_3 \sin \theta_{LR} - K_2 \sin \theta_{LT}) > 0$ in Equation (6), the following expression is derived:

$$\frac{\Delta l}{l} < 0. \quad (7)$$

The experimental results of $\Delta R/R < 0$ and $\Delta T/T > 0$ in Figure 1 require $\Delta l/l < 0$, that is, shows that the microfibril contracts along its longitudinal axis with NaOH treatment when Equations (1) to (3) are hold. The same result is also obtained from equation (1) because of $\Delta l/l \approx \Delta L/L < 0$ due to $K_1 \Delta m/m \approx 0$.

Crystallinity changes and the location of the crystalline region

The above discussion suggests that microfibril contraction is the primary factor of anisotropic changes in wood. These changes can also be correlated with observed changes in the crystallinity of the microfibril at NaOH concentrations greater than 0.10 (Fengel *et al.*, 1995). Figure 4 shows the relationship between crystallinity and dimensional changes along the longitudinal axis of samples. Changes were calculated based on the corresponding wet dimension at $[\text{NaOH}] = 0$. Contraction of the wood sample increased with decreasing crystallinity starting at $[\text{NaOH}] = 0.10$. The change shown in Figure 4 implies that a decrease in crystallinity causes contraction of the microfibril itself along the longitudinal axis, and hence an overall contraction of the sample along the longitudinal axis.

Two hypotheses can be considered for the location of the amorphous region created in the

microfibril by NaOH treatment. One hypothesis is that the amorphous region exists about the crystalline region as a square of side a few nm and expands with the cross section. The other hypothesis is that the amorphous region forms at defects along the longitudinal axis of the microfibril which exist by about 20 nm and extends with a length along the longitudinal axis. The 20-nm length has been confirmed by leveling-off degree of polymerization (LODP) experiments and X-ray diffraction (Hayashi *et al.*, 1989). The high linear correlation of $\Delta L/L$ as a function of crystallinity shown in Figure 4 suggests that NaOH treatment induces crystallinity changes in one of the aforementioned regions. Nakano *et al.* (2000) reported that this change in crystallinity is localized in the longitudinal region of microfibril rather than the cross section.

Figure 5 shows the proposed combination mode of crystallinity of microfibers after NaOH treatment, where the crystallinity along the longitudinal and cross-sectional axes are w_c and h_c , respectively. That is, they are the contribution of parallel and series to the longitudinal axis of microfibrils. The gross crystallinity, ζ , is represented by

$$\zeta = h_c \cdot w_c, \quad (8)$$

This equation should not be a linear function of [NaOH] if the both crystallinity w_c and h_c have a [NaOH] dependence. However, ζ as a function of NaOH concentration shows a highly correlated linear relationship, as shown in Figure 6. The crystallinity of wood samples ζ is approximately used as that of microfibrils in wood. This provides additional evidence that the crystallinity changes causes in either region of the both. Therefore, it can be concluded that exposure to aqueous NaOH induces changes in crystallinity along the longitudinal axis, which in turn induces microfibril contraction.

The crystallinity of the wood samples were determined from X-ray diffraction data obtained on the LR-plane at 30 kV, 100 mA, and 2 °/min. The degree of crystallinity was calculated from an the diffraction profile in the scanning range 10 – 32°.

242

243 **Estimation of the microfibril angle**

244

245 Substitution of Equation (1) into Equations (2) and (3) yields the following expressions
246 for $\Delta R/R$ versus $\Delta L/L$ and $\Delta T/T$ versus $\Delta L/L$, where $K_1 \Delta m/m$ is neglect because of
247 $K_1 \Delta m/m = 0.0010$:

$$248 \quad \frac{\Delta R}{R} = \phi \frac{\Delta L}{L} \sin \theta_{LR} + K_2(1-\phi) \frac{\Delta m}{m}, \quad (9)$$

$$249 \quad \frac{\Delta T}{T} = \phi \frac{\Delta L}{L} \sin \theta_{LT} + K_3(1-\phi) \frac{\Delta m}{m}. \quad (10)$$

250 Microfibril angles in the LR- and LT-planes can be calculated using the first derivatives of
251 Equations (9) and (10) as a function of $\Delta L/L$, which are confirmed by experimental results at
252 $[\text{NaOH}] > 0.10$ for $\Delta R/R$ versus $\Delta L/L$ and $\Delta T/T$ versus $\Delta L/L$. The second terms in both
253 equations are regarded as constant, since $\Delta R/R$ and $\Delta T/T$ are almost constant and $\Delta L/L = 0$
254 at $[\text{NaOH}] < 0.10$.

255 Experimental results yielded slope values of 0.0800 for $\Delta R/R$ versus $\Delta L/L$ and 0.0188
256 for $\Delta T/T$ versus $\Delta L/L$, with y -intercepts of 0.0045 and 0.0305, respectively. Accordingly,
257 microfibril angles of $\theta_{LR} = 9.20^\circ$ and $\theta_{LT} = 2.15^\circ$ were obtained. The former value agrees
258 reasonably well with the average microfibril angle observed in the LR-plane shown in Figure 2,
259 though the latter appears to be too little comparing the results reported (Nakato, 1958) In the
260 present report, these values were deemed valid and used in the below simulation.

261

262 **Simulation of the anisotropic dimensional change**

263

264 The main parameter affecting dimensional changes in the wood samples was
265 crystallinity changes as a result of the NaOH treatment shown in Figure 4. NaOH induces a
266 decrease in microfibril crystallinity, which causes contraction of the microfibril along the
267 longitudinal axis and ultimately a contraction of the wood sample along the longitudinal axis of
268 the sample. It should be noted that the longitudinal axis of microfibril differs from that of the
269 sample. Although this effect is manifest primarily along the longitudinal axis of the sample, the

tangential and radial regions are also considered in the below simulation.

From Equation (1), the dimensional change of the sample, $\Delta L/L$, with the experimentally derived $K_1 \Delta m/m = 0.0010$, can be represented by

$$\frac{\Delta L}{L} = \frac{\Delta l}{l} + 0.0010, \quad (11)$$

where the value 0.0010 represents the contribution of matrix swelling to the overall dimensional change of the sample along the longitudinal axis at $[\text{NaOH}] = 0.03$ to 0.07 and is negligible small. The value $\Delta L/L$ was calculated from the contraction of the microfibril, $\Delta l/l$, as shown in Equation (11). Thus, determination of $\Delta L/L$ can be reduced to $\Delta l/l$, which in turn can be evaluated from the end-to-end distance of the amorphous cellulose chain along the longitudinal axis of the microfibril.

It is difficult to know the actual behavior of the cellulose chain when both ends may be bound to a crystalline region, though some researchers reported the simulation of conformation of single cellulose chain in this regard (for example Queyroy et al., 2004). Additionally, the end-to-end distance of the cellulose chain appears to be slightly influenced by non-crystallization because of a non-flexible polymer chain. Therefore, the classical method by Benoit (1947), using the characteristic parameter α to represent a corrected deviation from the free jointed chain model, was utilized herein.

As well-known, the end-to-end distance of the cellulose chain is represented by $0.79\sqrt{N}$ for the unit number N when the appropriate constants are substituted in Benoit's equation: a C–O bond length of 0.143 nm, a length between C_1 and C_4 equal to 0.298 nm, and angles COC and C_1C_4O of 110° and 150° , respectively. Benoit's equation requires the correction term α , representing the length of the free jointed chain model. For example, α is typically 2–5 for cellulose tributylate and cellulose tricaplate and about 2 for polyethylene. The former values are representative of a rod-like polymer conformation and the latter has a simple, flexible structure. Thus, the length of the amorphous region along the longitudinal axis of microfibril l_a is described by $l_a = 0.79\alpha\sqrt{N}$.

The change in microfibril length, $\Delta l/l$, can be represented by the degrees of non-crystallization of microfibrils with NaOH treatment, with microfibril length, the length of a glucose residue, and crystallinity along the longitudinal axis given by l_u , l_g , and $h_c (= \zeta/w_c)$,

299 respectively:

$$300 \quad \frac{\Delta l}{l} = \left(l_u \cdot h_c + 0.79\alpha \sqrt{\frac{l_u(1-h_c)}{l_g}} \right) / l_u - 1 \quad (12)$$

301 The first and second terms in parentheses of Equation (12) are the length of the crystalline and
302 amorphous regions, respectively. The first term in Equation (12) is the ratio of microfibril
303 length after / before NaOH treatment. The microfibril length l_u is the period determined from
304 LODP and X-ray diffraction with 20nm. Substituting $l_u = 20$ nm and $l_g = 0.515$ nm into
305 Equation (12) and then substituting this result into Equation (11) yields

$$306 \quad \frac{\Delta L}{L} = \left[\left(20 \cdot h_c + 0.79\alpha \sqrt{\frac{l_u(1-h_c)}{0.515}} \right) / 20 - 1 \right] \cos \theta + 0.0010 \quad (13)$$

307 Dimensional changes in the wood samples as a function of crystallinity induced by
308 NaOH treatment can now be simulated using Equations (8) and (13). The simulation variables
309 were $h_c (= \zeta / w_c)$ and α , since the empirical microfibril angles were small ($\theta_{LR} = 9.20^\circ$ and $\theta_{LT} =$
310 2.15° so that $\cos \theta_{LR} \approx \cos \theta_{LT} \approx 1$). Typical results in Figure 7 show that the most accurate
311 simulations were obtained with $\alpha = 3$, when $w_c = 1.00$ and then $h_c (= \zeta / w_c) = 0.522$ where ζ the
312 gross crystallinity. This implies that changes in crystallinity occurred only along the
313 longitudinal axis of microfibrils and that the amorphous cellulose chains are extended.

314 Table 1 shows the results obtained with $\alpha = 2.5$ and 3. The degree of contraction
315 calculated from the ratio of end-to-end distance to contour length was about 0.10–0.20.
316 According to analyses of single cellulose chains by Queyroy *et al.* (2007), the end-to-end distance
317 of a chain consisting of eight glucose residues with a contour length of 4.4 nm is about 3.2 nm.
318 This corresponds to a 0.30 contraction. Considering $N = 13$ to 26 in this work and $N = 8$ in
319 Queyroy's simulation, the former is much smaller than the latter. This may simply result from
320 the different calculation methods employed. However, the most likely reason is that both ends
321 of the amorphous cellulose chains bond to the crystalline regions and are therefore unable to
322 satisfactorily contract. This conclusion is also supported by the simulation results obtained with
323 $\alpha = 3$.

324 The observed changes in the radial and tangential directions, $\Delta R / R$ and $\Delta T / T$, were
325 also simulated based on derivations from Equations (9) and (10). Simulation requires the
326 parameters K_1 and K_2 . Their contribution can be estimated using $\Delta R / R$ and $\Delta T / T$ at [NaOH]

< 0.10 since the microfibril does not contract at $[\text{NaOH}] < 0.10$, where dimensional changes are due to changes in the matrix only:

$$\frac{\Delta R}{R} = K_2(1-\phi) \frac{\Delta m}{m} \quad (14)$$

$$\frac{\Delta T}{T} = K_3(1-\phi) \frac{\Delta m}{m} \quad (15)$$

Both $\Delta T/T$ and $\Delta R/R$ varied little at $[\text{NaOH}] < 0.1$ and were regarded as constant. Empirical results were $\Delta R/R = K_2(1-\phi)\Delta m/m = -0.0037$ and $\Delta T/T = K_3(1-\phi)\Delta m/m = 0.0217$. Similarly, $K_1\Delta m/m = 0.0010$ was obtained from empirical result at $[\text{NaOH}] < 0.1$ and Equations (1). That is, K_1 and K_2 are almost 0 and $K_3 > 0$ at $[\text{NaOH}] < 0.1$, considering swelling of matrix. This fact suggests strong restraint along the longitudinal and radial axes and little restraint along tangential axis.

As shown in Fig.1, $\Delta T/T$ was constant swelling and $\Delta R/R$ varied little at $[\text{NaOH}]$ between 0.03 and 0.10 where no longitudinal shrinking. This fact suggests that wood matrix is only slightly dependent on NaOH concentration though it swells due to the NaOH treatment. Thus, assuming that dimensional changes in the wood matrix were constant over $[\text{NaOH}] = 0.03$ to 0.20, $\Delta T/T$ and $\Delta R/R$ were calculated using Equations (2) and (3). The most accurate results for $\Delta L/L$ were obtained with $\alpha = 3$, $h_c = 0.522$, $w_c = 1.00$, $\theta_{LT} = 2.15^\circ$, and $\theta_{LR} = 9.20^\circ$. These results are shown in Figure 1 as solids lines which are best fitting and show good agreement between experimental and calculation data. Some disagreement, however, can be observed along the tangential axis and may be due to the Poisson ratio effect, which was not accounted for in these simulations. Low microfibril angles allow the matrix to swell easily along the in tangential axis. Additional changes due to the Poisson effect may then be caused by shrinking along the radial axes. This effect may also contribute to the observed discrepancy between experimental and theoretical results in Figure 1 at $[\text{NaOH}] > 0.10$.

Conclusion

Anisotropic swelling of wood samples with treatment with aqueous NaOH solution at 0 to 0.20 fraction concentrations was examined. At NaOH concentrations less than 0.10, swelling

occurred only along the tangential axis (T) and not along the radial (R) or longitudinal (L) axes. At greater NaOH levels, the swelling was even more pronounced along T, with shrinkage along the other axes. These anisotropic changes along R and L were closely related to the longitudinal crystallinity change of microfibrils in the wood cell wall and were simulated with the cell structure model. This exercise revealed microfibril contraction and matrix swelling in the wood cell wall upon NaOH treatment. That is, the characteristic dimensional changes in wood with NaOH treatment are due to the decreasing crystallinity of microfibrils, matrix swelling, and differences in microfibril angles in the LP[±] and LT[±] planes of the wood cell wall. The main factor is microfibril contraction along the longitudinal axis with decreasing crystallinity in the microfibrils. The results obtained in this analysis illustrate the complex interaction between microfibrils and the matrix and may serve as a new basis for understanding the anisotropic swelling and shrinkage of wood.

Acknowledgements

The author would like to thank Dr. Ishikura at the Hokkaido Forest Research Institute for agreement with use in this work of our data and Assistant Prof. Awano at Kyoto University for measuring the microfibril angle of the samples.

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Figure captions

Fig. 1. Experimental (plots) and best fitting (solid lines) results of dimensional changes along the radial (\square), tangential (\square), and longitudinal (\circ) axes as functions of the NaOH aqueous solution. Note: $\alpha = 3$, $\theta_{LT} = 2.15^\circ$ and $\theta_{LR} = 9.20^\circ$.

Fig. 2. Dependence of microfibril angle on the concentration of aqueous NaOH solution.

Fig. 3. The cell wall model for anisotropic dimensional changes consisted of matrix and microfibril components. Note: θ = fibril angle, φ = volume fraction of the microfibril.

Fig. 4. Dimensional changes along the longitudinal axis of treated wood as functions of crystallinity.

Fig. 5. A schematic diagram for the crystalline and amorphous regions of a microfibril.

Note: w_c and h_c are crystallinity of micro fibril in cross section and longitudinal directions.

Fig. 6. Relationship between crystallinity and concentration of aqueous NaOH solution for Yezo spruce treated with aqueous NaOH solution.

Fig. 7. Typical experimental (open circle) and simulated (solid line) results of dimensional changes along the longitudinal axis of wood samples. Note: θ = fibril angle; α = characteristic ratio; w_c = crystallinity of the cross section.

Table 1. Typical end-to-end distances, representing the highest degree of agreement between experimental and theoretical results in amorphous regions of 20-nm microfibrils.

Note: w_c = crystallinity of the cross-sectional area; h_c = crystallinity of the longitudinal area; N = number of glucose residues in the amorphous region; α = characteristic ratio.

Crystallinity ζ	$w_c = 1.00$			$w_c = 0.70$		
	h_c	N	$\alpha=3$ Distance (nm)	h_c	N	$\alpha=2.5$ Distance (nm)
0.459	0.459	21	10.9	0.656	13	7.2
0.428	0.428	22	11.2	0.611	15	7.7
0.380	0.380	24	11.6	0.543	18	8.3
0.351	0.351	25	11.9	0.501	19	8.7
0.320	0.320	26	12.2	0.457	21	9.1

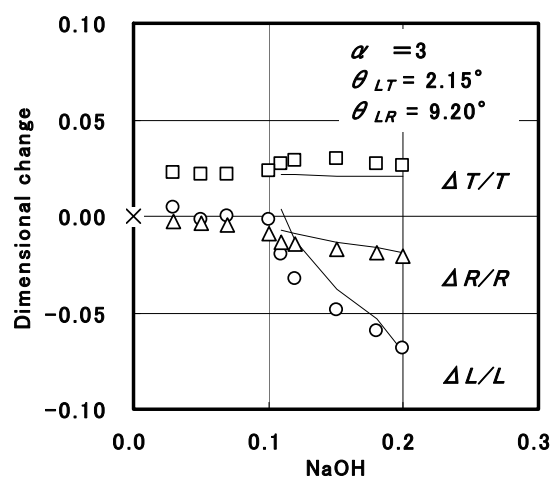


Fig. 1. Experimental (plots) and best fitting (solid lines) results of dimensional changes along the radial (\square), tangential (\triangle), and longitudinal (\circ) axes as functions of the NaOH aqueous solution. Note: α (characteristic ratio of polymer conformation)= 3, $\theta_{LT} = 2.15^\circ$ and $\theta_{LR} = 9.20^\circ$.

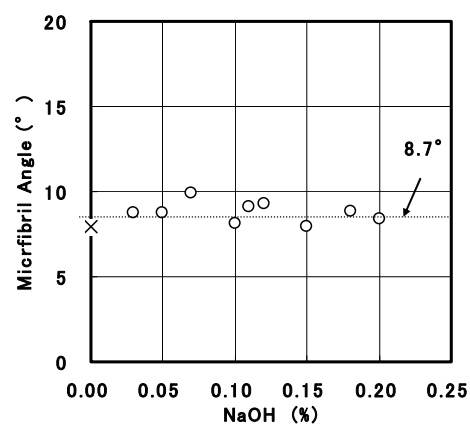


Fig. 2. Dependence of microfibril angle on the concentration of aqueous NaOH solution.

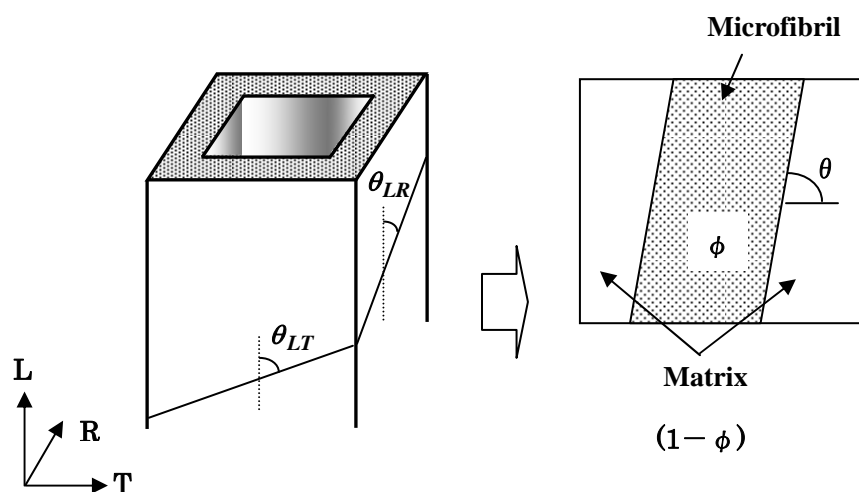


Fig. 3. The cell wall model for anisotropic dimensional changes consisted of matrix and microfibril components. Note: θ = fibril angle, ϕ = volume fraction of the microfibril.

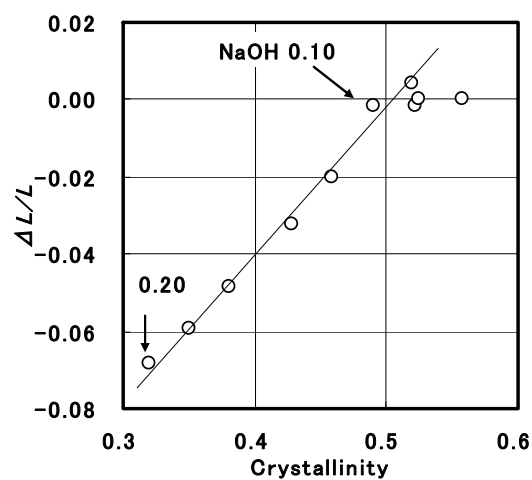


Fig. 4. Dimensional changes along the longitudinal axis of treated wood as functions of crystallinity.

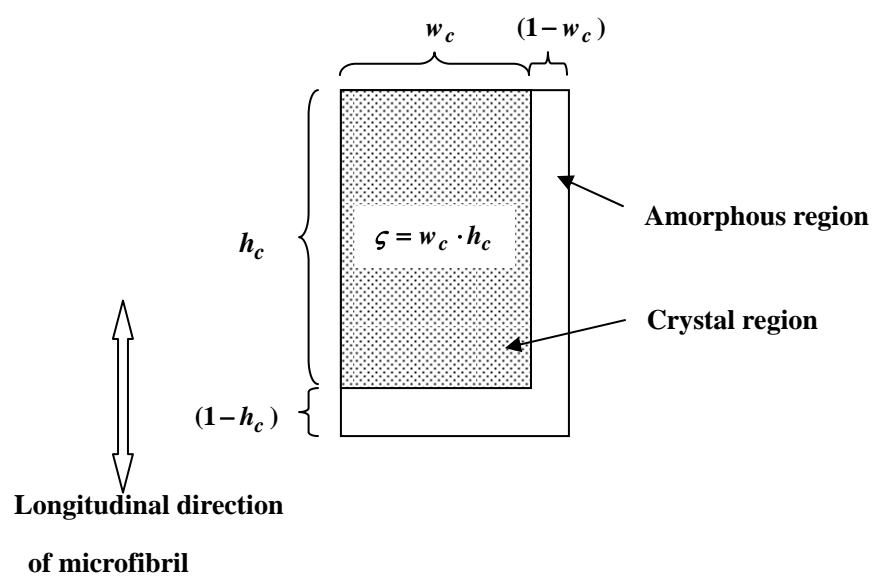


Fig. 5. A schematic diagram of combination mode for the crystalline and amorphous regions of a microfibril. Note: w_c and h_c are crystallinity of micro fibril in cross section and longitudinal directions.

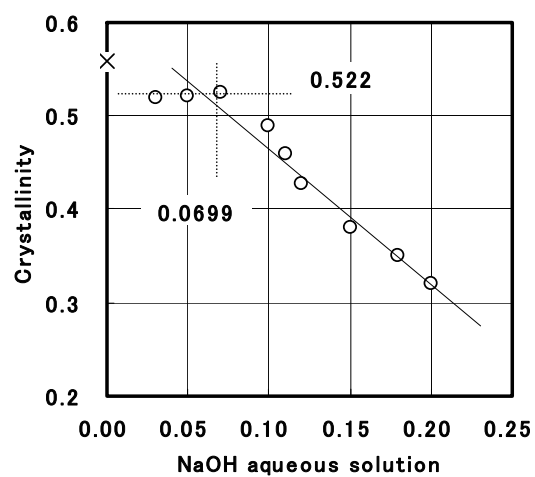


Fig. 6. Relationship between crystallinity and concentration of aqueous NaOH solution for Yezo spruce treated with aqueous NaOH solution.

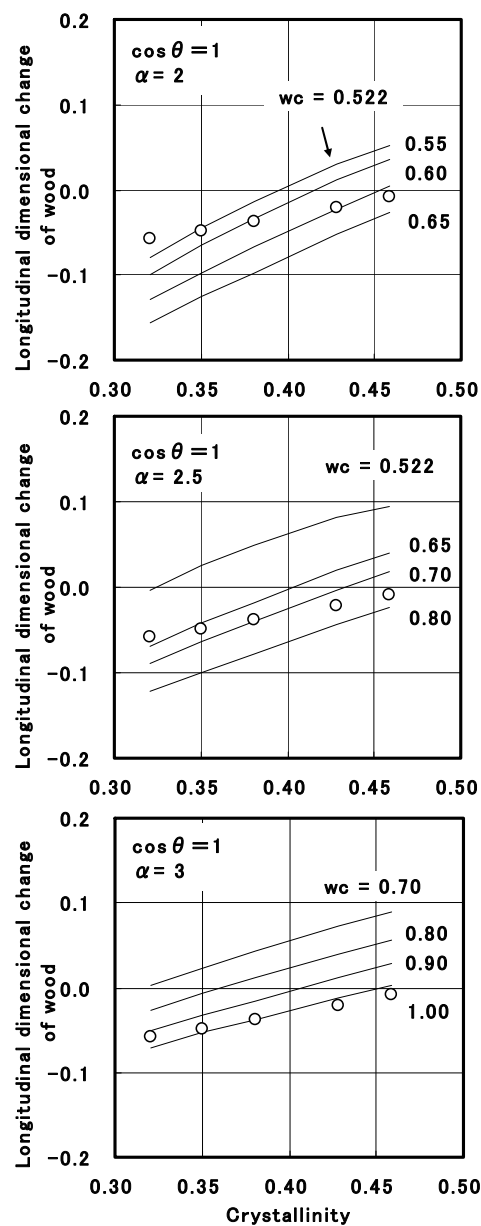


Fig. 7. Typical experimental (open circle) and simulated (solid line) results of dimensional changes along the longitudinal axis of wood samples. Note: θ = fibril angle; α = characteristic ratio; w_c = crystallinity of the cross section.